

Preparation of Some Novel Triorganodichlorostannate Complexes

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As part of a programme to prepare water soluble tributyltin salts as biocides for wood preservation,¹ we have investigated the formation of complexes containing the tributylidihalogenostannate anion, $(\text{Bu}_3\text{SnX}_2)^-$, where X = Cl, Br or I, and now report the preliminary results of our findings.

Previous work has shown that trimethyl-,² triethyl-,³ and triphenyltin⁴ halides take up halide ion to form anions, of the type $(\text{R}_3\text{SnX}_2)^-$, where the tin atom is five coordinate and occupying a trigonal bipyramidal geometry.^{3,5} Tri-n-butyltin halides are weaker Lewis Acids, and, although known to form 1:1 adducts of low stability with neutral monodentate donor ligands⁶ (e.g. $\text{Bu}_3\text{SnCl}\cdot\text{py}$), no complexes containing the tributylidihalogenostannate anion, $(\text{Bu}_3\text{SnX}_2)^-$, have been reported. On the other hand, the dibutyltin dihalides and the monobutyltin trihalides, which are stronger Lewis Acids than their tributyltin counterparts, form well-defined complexes, $(\text{R}_4\text{N})_2^+(\text{Bu}_2\text{SnX}_4)^{2-}$ and $(\text{R}_4\text{N})_2^+(\text{BuSnX}_5)^{2-}$ respectively, where R = Me or Et, X = Cl, and these may be isolated as stable crystalline solids.^{7,8}

Results and Discussion

When equimolar quantities of tributyltin chloride and benzyltriphenylphosphonium chloride were mixed in methanol or isopropyl alcohol and left to stand at room temperature for 1–2 days, colourless crystals of $(\text{PhCH}_2\text{PPh}_3)^+(\text{Bu}_3\text{SnCl}_2)^-$, m.p. 115–8 °C, separated in 60% yield. These were stable in air and appear to be the first example of a solid complex containing the tributylidihalogenostannate anion. Tripropyl- and tribenzyltin chlorides also reacted with benzyltriphenylphosphonium chloride under similar conditions, to furnish the new crystalline complexes, $(\text{PhCH}_2\text{PPh}_3)^+(\text{Pr}_3\text{SnCl}_2)^-$, m.p. 117–20 °C and $(\text{PhCH}_2\text{PPh}_3)^+(\text{PhCH}_2)_3\text{SnCl}_2)^-$, m.p. 73–5 °C, in good yields. Satisfactory analytical data were obtained for all compounds.

Tributyltin bromide or iodide did not form tributylidihalogenostannate complexes, $(\text{PhCH}_2\text{PPh}_3)^+(\text{Bu}_3\text{SnX}_2)^-$, where X = Br or I, with benzyltriphenyl-

TABLE. Infrared Tin–Chlorine Stretching Frequencies of $(\text{R}_3\text{SnCl}_2)^-$ Anions.

Compound	$\nu(\text{Sn}-\text{Cl})^a$ cm ⁻¹
Me_3SnCl	325 ^b
Et_3SnCl	326 ^d
Pr_3SnCl	324
Bu_3SnCl	322
$(\text{PhCH}_2)_3\text{SnCl}$	299
Ph_3SnCl	344 ^f
$(\text{Et}_4\text{N})^+(\text{Me}_3\text{SnCl}_2)^-$	225 ^c
$(\text{PhCH}_2\text{PPh}_3)^+(\text{Et}_3\text{SnCl}_2)^-$ ^e	230
$(\text{PhCH}_2\text{PPh}_3)^+(\text{Pr}_3\text{SnCl}_2)^-$	238
$(\text{PhCH}_2\text{PPh}_3)^+(\text{Bu}_3\text{SnCl}_2)^-$	222
$(\text{PhCH}_2\text{PPh}_3)^+(\text{PhCH}_2)_3\text{SnCl}_2)^-$	226
$(\text{Me}_4\text{N})^+(\text{Ph}_3\text{SnCl}_2)^-$	240 ^f

^a Nujol mulls (except R_3SnCl , R = Me, Et, Pr or Bu, which are liq. films). ^b Ref. 9. ^c Ref. 2. ^d Ref. 10. ^e M.p. 189–90 °C (not quoted in ref. 3). ^f Ref. 11.

phosphonium bromide or iodide and only starting materials were recovered. Attempted reaction of various tetra-alkylammonium chlorides, $\text{R}_3\text{R}'\text{N}^+\text{Cl}^-$ (R = R' = Me or Et; R = Me or Et, R' = PhCH_2), with tributyltin chloride also returned only starting materials.

The tin–chloride stretching frequencies in the far infrared spectra of the $(\text{R}_3\text{SnCl}_2)^-$ anions are found to be lowered by some 100 cm⁻¹ compared with those of the parent R_3SnCl compounds, due to an increase in the coordination number of the tin atom from four to five on complexation (Table).

Although the aqueous solubility of these particular compounds is low, the fact that such complexes can be prepared is encouraging and further studies are now under way to determine the effect of cation size on the stability and solubility of the $(\text{R}_3\text{SnX}_2)^-$ anions.

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